

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 30, NO. 1, AUG. 1960

EFFECT OF PLASTIC DEFORMATION ON IONIC  
CONDUCTIVITY OF SILVER CHLORIDE

BY KİYOSHI SHIMIZU

(Received June 30, 1960)

Plastic deformation of AgCl crystal at room temperature produced a conductivity increase that varied with strain. The conductivity increase recovered slowly at temperatures of the extrinsic range. The conductivity increase was mainly ascribed to the increase of the concentration of silver ion vacancies freed by the breaking up of the complexes associated with multivalent metallic impurities and produced by moving dislocations, and the recovery was attributed to the bimolecular reaction between the silver ion vacancies and the traps. For thoroughly recovering the conductivity increase, it was necessary to anneal the deformed crystal at higher temperatures. In the range of these temperatures, the recovery of the conductivity increase corresponded to the disappearance of the birefringent bands.

## Introduction

It is well known that the darkenability of color centers in alkali halide increases by the plastic deformation. The same phenomena<sup>1)</sup> are observed in the silver chloride crystal. In the cold worked crystal, silver colloids produced at the surfaces by the photolysis diffuse into the crystal and disperse in smaller particle size at the moderate temperature (200°~300°C). But, in the annealed crystal the silver colloids are rather bleached to some extent. From the above, we may expect that the plastic deformation would produce in the crystal many defects, such as vacancies, interstitial ions and dislocations, which are favorable to the dispersion of silver colloids. These defects are also important factors for the ionic conductivity at temperature of the extrinsic region so that the plastic deformation produces some effects that might lead to an increase in the ionic conductivity. The ionic conductivity  $\sigma$  is often given by the following formula,

$$\sigma = neu_0 \exp(-E/kT) \quad (1)$$

where,

$n$ , concentration of charge carriers

$e$ , charge of an electron

$u_0$ , constant

$E$ , activation energy of mobility

$k$ , Boltzmann constant

$T$ , absolute temperature

and  $n$  and  $E$  may be the functions of degree of cold-work and of time of annealing.

1) R. Kiyama and K. Shimizu, *This Journal*, 25, 41 (1955)

In the problem of the variation of the ionic conductivity by plastic deformation, investigators have not always been in accord as well for the experimental results as their interpretations. Gyulai and Hartly<sup>2)</sup> observed for the first that the conductivity of sodium chloride was increased by a factor of 10 to 100 by plastic deformation at the ordinary temperature. This increase decayed rapidly with the lapse of time. Seitz<sup>3)</sup> interpreted the results of Gyulai and Hartly as an enhancement of the ionic conductivity resulting from the production of free lattice vacancies by moving dislocations during the deformation and as the decay being due to the association of the positive and negative ion vacancies. Recently, Johnston<sup>4)</sup> found that the plastic deformation of silver bromide at and below room temperature produced a conductivity increase that varied linearly with strain and Burmeister<sup>5)</sup> studied the effect of plastic deformation on the conductivity of the potassium chloride containing calcium ions. These authors attributed the conductivity increase to a low activation energy in the regions of disorder (groups of dislocations) that were introduced by the deformation.

Now, the author has investigated the effect of plastic deformation on the ionic conductivity of silver chloride crystal in reference to the optical results<sup>1)</sup> and observed the conductivity increase by deformation and its recovery at temperatures of the extrinsic range.

### Experimentals

AgCl was prepared by precipitation from purified ammoniac  $\text{AgNO}_3$  and HCl solutions.

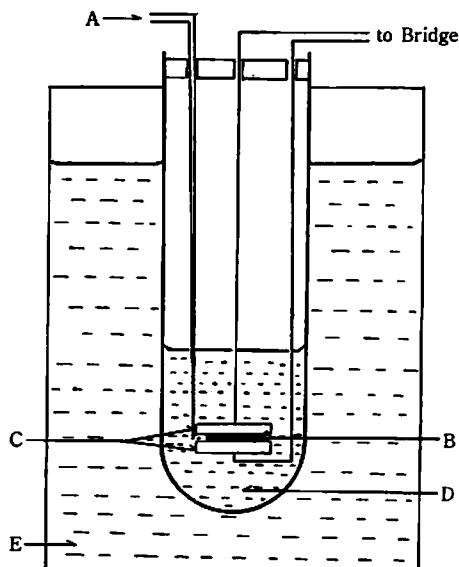


Fig. 1 Apparatus for measuring a.c. conductivity

- A—thermocouple
- B—specimen crystal
- C—electrodes
- D—silicone oil bath
- E—temperature bath

- 2) Z. Gyulai and D. Hartly, *Z. Physik*, **51**, 378 (1928)
- 3) F. Seitz, *Phys. Rev.*, **80**, 239 (1950)
- 4) W. G. Johnston, *ibid.*, **98**, 1777 (1955)
- 5) J. Burmeister, *Z. Physik*, **140**, 402 (1957)

AgCl precipitate was digested with HCl, washed with voluminous water and dried at 130°C.

Single crystal was grown by Kyropoulos' method and annealed at 400°C for 10 hours. In order to obtain the specimen for this investigation, the plates of AgCl crystal were sawn from the same crystal block with the saw blade of tungsten-steel. The surface of the plate was removed with a  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Then, the specimen was finished in dimensions of  $1 \times 5 \times 8$  mm with a glass plate and a  $\text{Na}_2\text{S}_2\text{O}_3$  solution. After finishing, the specimens were annealed at 400°C for 10 hours and cooled very slowly in the furnace.

Conductivity measurements were made in a silicone oil bath by means of a capacitance bridge at 1,000 cps as shown in Fig. 1. Electrodes were applied with silver paint.

Plastic deformation was given by a vice with a displacement indicator at room temperature (about 15°C), and it was checked by polarized light if the strain had been given homogeneously. It was one hour before the conductivity measurement was commenced.

All the manipulation was performed under the photochemically inactive light.

## Results

The ionic conductivity is characterized by the variation of temperature. As shown in Fig. 2, there were two ranges of temperature for the curve of conductivity  $\sigma$  and the plots of  $\log \sigma$  against the reciprocal of the absolute temperature  $1/T$  gave straight lines in both ranges. In the range of high temperature, the conductivity did not exhibit the individuality of the specimens, that is intrinsic, but, the conductivity depended on the history of the specimens in the range of low temperature, that is extrinsic. Below 50°C the polycrystal\* had a higher conductivity than

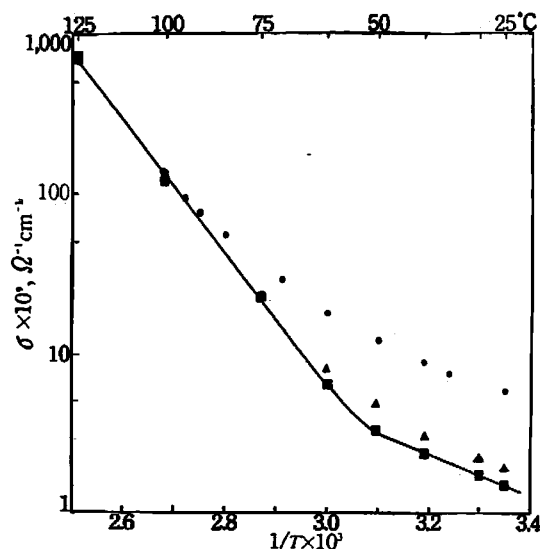


Fig. 2 Conductivity of annealed crystal of AgCl

- single crystal No. 1
- ▲ single crystal No. 2
- polycrystal

\* Polycrystal was prepared by casting the melt of single crystal No. 1. Conductivity did not change before and after annealing at 400°C for 5 hours.

the single crystals do and there was some variation between the single crystal No. 1 and No. 2. The slope of  $\log \sigma \sim 1/T$  curve gives the activation energy of mobility as mentioned in the introduction. The activation energies are 0.83 eV in the intrinsic range and 0.27 eV in the extrinsic range respectively. The activation energy in the extrinsic range did not differ among the specimens. These values are in good agreement with the result of Koch and Wagner<sup>6)</sup>.

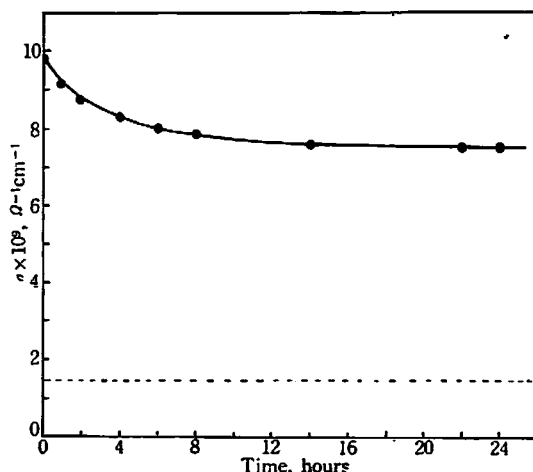


Fig. 3 Conductivity increase of AgCl by 17% plastic deformation and recovery at 25°C

Dotted line shows the conductivity before deformation.

In Fig. 3 is shown the conductivity increase by plastic deformation and its recovery. The conductivity was increased remarkably by plastic deformation. Its recovery at first proceeded rapidly, but the rate decreased gradually with the lapse of recovering time. After 24 hours' recovery, the conductivity was almost constant.

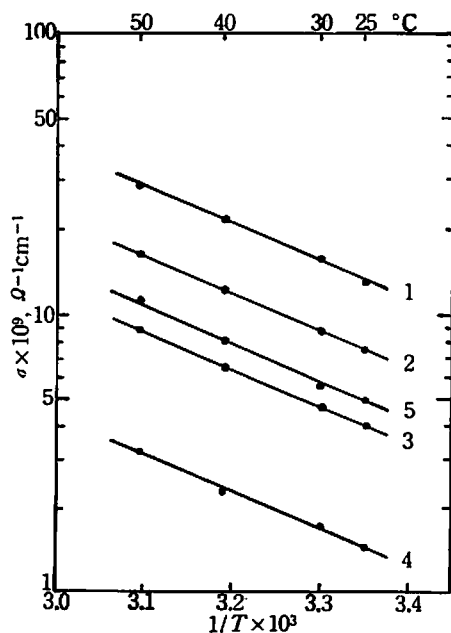


Fig. 4 Strain dependence of conductivity increase after 24 hours' recovery at 25°C

curve 1—30% strained single crystal  
2—17% "  
3—8% "  
4—undeformed single crystal  
5—undeformed polycrystal

6) E. Koch and C. Wagner, *Z. phys. Chem.*, 38 B, 295 (1937)

The conductivity was increased with increasing strain and in Fig. 4 is shown the strain dependence of the conductivity increase after 24 hours' recovery at 25°C. As  $\log \sigma \sim 1/T$  curves in deformed specimens have the same slope as the undeformed specimen, this indicates that the activation energy does not depend on the degree of strain.

As mentioned above, the conductivity increase produced by plastic deformation recovered slowly at temperatures of the extrinsic range. Fig. 5 shows the recovery of the specimens at 25°, 30° and 40°C which were given 17% deformation at 15°C. The rate of recovery increased with increasing temperature and decreased with the lapse of time at each temperature. In each case, the recovery did not particularly proceed after 8 hours' recovery.

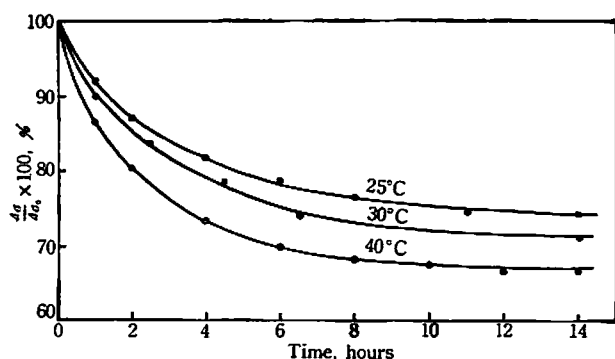


Fig. 5 Recovery of conductivity increase at various temperature

$\Delta\sigma_0$ —increment of conductivity at recovery time  $t=0$   
 $\Delta\sigma$ —increment of conductivity at recovery time  $t=t$

In Fig. 6 are shown the  $\log \Delta\sigma \sim 1/T$  curves at some recovery states. The temperature dependence of the conductivity increase was equivalent through the recovery process. This indicates that the activation energy does not vary with the degree of recovery and the activation energy was equal to the undeformed specimen.

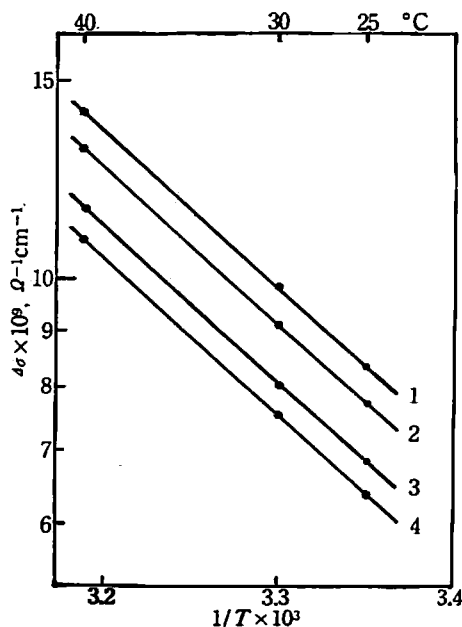


Fig. 6 Conductivity increase at various recovery states in 17% deformed specimen

curve 1— 0% recovery

2— 7.3% "

3— 18.0% "

4— 23.5% "

After 24 hours' recovery at temperatures of the extrinsic range, the specimens were observed qualitatively with polarized light. The birefringent bands of these specimens did not differ so much from those in the initial state. These specimens were annealed at 200°C for 5 hours, but the bands did not disappear thoroughly and some bands remained. For thorough disappearance, it required 5 hours' annealing at 400°C. In Fig. 7 is shown the recovery of the conductivity

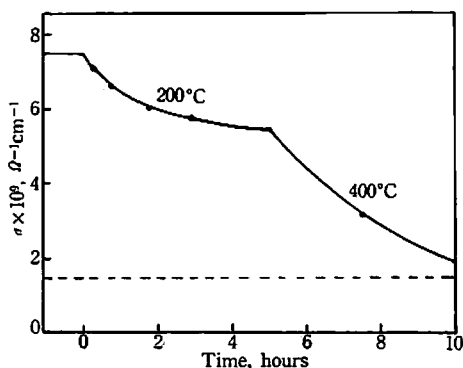


Fig. 7 Recovery of conductivity increase at high temperatures

Dotted line shows the conductivity before deformation.

at high temperatures corresponding to the above mentioned optical observation. The measurements were made at 25°C. The conductivity was decreasing with the lapse of annealing at 200°C, but the increment of conductivity  $\Delta\sigma$  considerably remained after 5 hours. At last, this conductivity recovered by annealing at 400°C for 5 hours. The degree of the recovery of the conductivity roughly corresponded to that of the disappearance of the birefringent bands.

### Considerations

It has been considered that in the silver halide crystal the predominant lattice defect is the Frenkel defect, consisting of a silver interstitial ion and a silver ion vacancy, and that the silver ion vacancy must play a key part in the diffusion process at the temperatures of the extrinsic range<sup>7)</sup>. As mentioned in the introduction, at a constant temperature the conductivity is a function of the concentration of charge carriers and the activation energy of the mobility which might be influenced by plastic deformation. But the experimental results showed that the activation energy of the mobility of the deformed crystal did not vary with the degree of strain and the degree of recovery and its value was equal to that of the undeformed crystal. Therefore, the conductivity increase by plastic deformation should be attributed to the increase of the concentration of charge carriers and the charge carriers in the deformed crystal would also mainly consist of the silver ion vacancies, which were freed by breaking up the complexes associated with multivalent metallic impurities by moving dislocations and produced by the moving of dislocations during the plastic deformation. This assumption does not seem unreasonable, as the concentration of impurities would not be more than about  $10^{15} \sim 10^{16}/\text{cm}^3$  even if the conductivity increase is entirely ascribed to the silver ion vacancies freed by breaking up the associated complexes, and also it is considered

7) W. D. Compton and R. J. Maurer, *J. Phys. Chem. Solids*, **1**, 191 (1956)

that the energy of formation of vacancy would be, as a rule, smaller than that of interstitial ion by the moving dislocations.

In the process of recovery at temperatures of the extrinsic range, the recovery of the conductivity increase may be due to the recombination of the silver ion vacancies with other imperfections, 'traps', and this process may be treated as the bimolecular reaction between the silver ion vacancy and the traps. Namely, the rate of decreasing of the concentration of silver ion vacancies,  $-\frac{dn}{dt}$  is given by the following equation:

$$-\frac{dn}{dt} = knn_t = kn(n_{ti} - n_t + n), \quad (2)$$

where  $n$  is a concentration of silver ion vacancies;  $n_t$  is a concentration of traps;  $k$  is a rate constant;  $t$  is a recovery time; and suffix  $i$  indicates the initial state ( $t=0$ ). The solution of Equation (2) is

$$n = \frac{n_t - n_{ti}}{1 - \frac{n_{ti}}{n_t} \exp(-(n_t - n_{ti})kt)}. \quad (3)$$

It follows, from  $n_t - n_{ti} = n_\infty$ , that

$$1 - \frac{n_\infty}{n} = \frac{n_{ti}}{n_t} \exp(-n_\infty kt) = A \exp(-k't), \quad (4)$$

where  $A = n_{ti}/n_t$ , and  $n_\infty k = k'$ .

Now, as the conductivity is proportional to the concentration of silver ion vacancies, Equation (4) can be put into the form

$$1 - \frac{\sigma_\infty}{\sigma} = A \exp(-k't) \quad (5)$$

with  $\frac{n_\infty}{n} = \frac{\sigma_\infty}{\sigma}$ .

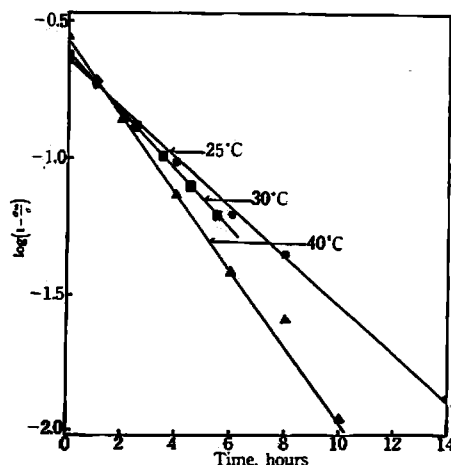


Fig. 8 Relation between  $\log(1 - \frac{\sigma_\infty}{\sigma})$  and recovery time

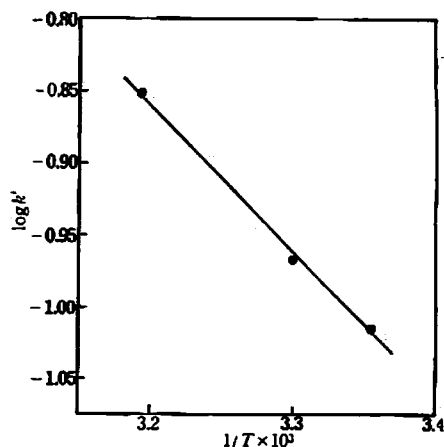


Fig. 9 Relation between  $\log k'$  and  $1/T$

$\log\left(1 - \frac{\sigma_{\infty}}{\sigma}\right)$  is a linear function of recovery time  $t$  and the slope of  $\log\left(1 - \frac{\sigma_{\infty}}{\sigma}\right) \sim t$  curve gives the value of  $k'$ .

In Fig. 8, the experimental results of  $\log\left(1 - \frac{\sigma_{\infty}}{\sigma}\right)$  are plotted against recovery time  $t$ . The plots are linear and can be fitted with Equation (5). Then, the values of  $k'$  are calculated from the slopes of the straight lines in Fig. 8. The plot of  $\log k'$  against the reciprocal of the absolute temperature  $1/T$  is shown in Fig. 9. The plot is linear and its slope gives the apparent activation energy of 0.20 eV, supposing that the  $n_{\infty}$  does not vary with recovering temperature.

It may be considered that there are four possibilities as the traps for the recombination of silver ion vacancies, 1) silver interstitial ions, 2) chlorine ion vacancies, 3) multivalent metallic impurities and 4) jogs of dislocations. In comparison with the activation energy obtained in this experiment, the activation energy would be smaller in the case of recombination of silver ion vacancies with silver interstitial ions<sup>8)</sup> and larger in the case of recombination with chlorine ion vacancies.

It would be expected that the jogs of dislocations are good traps of silver ion vacancies. But according to the optical results of the silver colloids<sup>1)</sup>, the deformed crystal provided many good traps, which would be the jogs, for the formation of colloids even after long recovery time at room temperature, and in order to annihilate the traps, it was necessary to anneal the deformed crystal for a long time at temperatures of the intrinsic range. The same heat treatment was also necessary for the disappearance of the birefringent bands corresponding with the recovery of the conductivity increase. Therefore, the jogs would not play an important part for traps in this recovery process, but in the process of recovery at higher temperatures.

It is reasonable to consider that this process would be mainly due to the recombination of silver ion vacancies with multivalent metallic impurities. In alkali halide crystals, the activation energy for association of positive ion vacancies with divalent impurities is about 0.4 eV<sup>5,9)</sup>. As the dielectric constant for silver chloride is about two fold larger than that of alkali halide (12.3 for AgCl, in contrast with 5.62 for NaCl and 4.68 for KCl), it can be roughly estimate that the activation energy in the case of silver chloride is about a half of that alkali halide and the value is in good agreement with the experimental result, 0.20 eV.

The author has great pleasure in expressing his sincere thanks to Prof. Wasaburo Jono for his valuable guidance and encouragement during the course of the investigation.

*The Laboratory of Physical Chemistry  
Kyoto University  
Kyoto, Japan*

8) F. Seitz, *Rev. Mod. Phys.*, **23**, 328 (1951)

9) D. B. Fischbach and A. S. Nowick, *J. Phys. Chem. Solids*, **2**, 226 (1957)

F. Bassani and F. G. Fumi, *Phil. Mag.*, **45**, 228 (1954)